

PATENT SPECIFICATION (11)

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- (21) Application No. 34807/73 (22) Filed 20 July 1973 (19)
 (23) Complete Specification filed 15 July 1973
 (44) Complete Specification published 18 Feb. 1976
 (51) INT. CL.² C08G 18/28 B32B 27/40
 (52) Index at acceptance
 C3R 32D14 32D16A 32D16C 32D6A 32D6C 32D6J 32D6K
 32G2B 32H5B2 32H5BY 32H8 32J2F 32J2Y 32KL
 (72) Inventors DAVID ADSLEY and HENRY FRANCIS CHRISTMAS



(54) IMPROVEMENTS IN AND RELATING TO PRESSURE-SENSITIVE ADHESIVES

- (71) We, ADHESIVE TAPES LIMITED, a British Company of 1 Redcliffe Street, Bristol, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to provision of a pressure-sensitive adhesive as a layer upon a suitable substrate such as paper or cloth fabric, or a thin plastics sheet.
- By a "pressure-sensitive adhesive" as used in this Specification is meant a reaction product which remains tacky over a wide range of temperatures, viz. at least $-20^{\circ}\text{C}.$ to $70^{\circ}\text{C}.$, and which will adhere to most surfaces when light pressure is applied at ambient 285 chain atoms. The term chain-length is defined in that earlier work as follows:—
- By the term "chain-length" as used in this Specification there is meant the length of a chain in terms of chain-atoms as measured from the point of attachment of a chain branching therefrom, to an adjacent point of attachment of a further chain branching from the first-mentioned chain, or as measured from the point of attachment of a chain branching from the first-mentioned chain to the end of the first-mentioned chain if the first-mentioned chain is free from attachments at one end.
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By a "pressure-sensitive adhesive" as used in this Specification is meant a reaction product which remains tacky over a wide range of temperatures, viz. at least $-20^{\circ}\text{C}.$ to $70^{\circ}\text{C}.$, and which will adhere to most surfaces when light pressure is applied at ambient temperatures in the absence of heat, moisture and other agents.

At the present time most pressure-sensitive adhesives are applied to a substrate in solution in a volatile solvent which is then removed by evaporation leaving the adhesive film on the substrate. Such a process is costly in that the rubbery or resinous adhesive components have to be dissolved or dispersed in the solvent, which itself can be a lengthy process, and in that solvent recovery has to be employed for environmental and economic reasons.

It has already been proposed to form pressure-sensitive adhesives of the polyurethane type from polyisocyanates and triols or mixtures of triols with diols and/or mono-ols. The polyols, according to the prior proposal, have to be reacted with sufficient isocyanate to give a fully cross-linked polymer and the average chain length should be 130—285 chain atoms. In triol/diol mixtures the molecular weight of the triol should be 100—500 and that the diol 1000—3000. If the triol is used alone it should have a molecular weight of 4000—8000.

Subsequent developments suggested the use of hydroxy-terminated or isocyanate-terminated pre-polymers and also suggested that the chain length might extend to be-

yond 285 chain atoms. The term chain-length is defined in that earlier work as follows:—

By the term "chain-length" as used in this Specification there is meant the length of a chain in terms of chain-atoms as measured from the point of attachment of a chain branching therefrom, to an adjacent point of attachment of a further chain branching from the first-mentioned chain, or as measured from the point of attachment of a chain branching from the first-mentioned chain to the end of the first-mentioned chain if the first-mentioned chain is free from attachments at one end.

The term "chain-atoms" refers only to the atoms in the main chain and does not include branch-chain atoms.

In one aspect the present invention provides a pressure-sensitive adhesive comprising a partially cross-linked polyurethane reaction product between one or more diols and/or higher polyols, preferably triols, terminated with primary and/or secondary hydroxyl groups and an organic polyisocyanate, preferably diisocyanate used in less than a stoichiometric amount, the chain length of the polyurethane reaction product being less than 130 chain atoms.

Usually at least 80% e.g. 85%—95% of the said stoichiometric amount will be used in the practice of this invention.

While any chain length below 130 is possible a chain length of 38—125 chain atoms gives useful results.

The preferred polyisocyanate is the toluene diisocyanate known as TDI. This is a mixture of the 2,4- and 2,6- isomer. Other aliphatic or aromatic polyisocyanates e.g. 4,4'-diisocyanatodiphenylmethane, hexamethylene diisocyanate, triphenylmethyl triisocyanate, 2,4,4'-triisocyanatotriphenyl ether and polymethylene polyphenyl isocyanate can also be utilised.

Usually a catalyst, i.e. accelerator, such as a metal carboxylate is added to the reaction mixture prior to curing. Examples are

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dibutyl tin dilaurate, stannous octoate or lead octoate.

The polyols employed in this invention may be hexols, e.g. sorbital, pentols, e.g. arabitol, tetrols, e.g. pentaerythritol, or triols, e.g. glycerol. Also, reaction products of these polyols and propylene oxide and/or ethylene oxide may be used in place of the unmodified polyols, a typical triol being a reaction product of glycerol and propylene oxide. Examples of diols which can be employed are poly(ethylene glycol) and poly(propylene glycol).

The proportion of reactants giving optimum pressure-sensitive adhesive properties depends partly on the particular diols and triols employed, especially with reference to whether the termination is by primary or secondary hydroxyl. One surprising feature which has been noted is that a different diol:triol balance is needed to generate a particular chain atom length, depending on whether the polyols are primary or secondary hydroxyl terminated. In general the chain atom length, corresponding to the degree of chain branching, will be regulated by using as polyol a corresponding proportion of diol and triol, the diol suitably having a molecular weight of 1000-3000 and the triol a molecular weight of 300-600. Under such conditions the higher the diol:triol molar ratio, other things being equal, the higher the chain length. In general, a molar ratio of diol to triol of 2:1 and below is useful for chain lengths below 130. However, using triol alone it has been found that a satisfactory product of the desired chain atom length can be formed using triols of substantially higher molecular weight.

Curing times will generally range from 3 to 20 minutes and temperatures from 60° to 200°C.

Polyols terminated with primary hydroxyl groups have the particular advantage in the process of this invention that in the presence of the organo-tin catalyst and at a temperature of 80°C, reaction speed with TDI is such that the reaction can be completed in about 10 minutes after which time no further free isocyanate can be detected by I.R. spectroscopy.

Another aspect of the present invention is a pressure-sensitive adhesive material consisting of the adhesive as described above coated onto a suitable substrate, e.g. of fabric, paper or (especially) polymer film, particularly when this is in the form of a tape.

Yet another aspect of the invention is constituted by a method of producing such a pressure-sensitive material wherein said one or more diols and/or higher polyols and the said polyisocyanate, together with any catalyst are applied as a mixture to at least

one surface of the substrate and caused or allowed to cure.

One advantage of this method is that continuation of the polymer formation will then take place on the substrate without the need for solvent recovery. Another advantage is that pressure-sensitive adhesives can readily be produced which do not require the addition of tackifying resins.

The following Examples illustrate how the invention may be carried into effect:

EXAMPLE 1

3.15 grams of ethylene oxide capped pro-molecular weight 2000 and 0.91 grams of a propylene oxide triol of molecular weight 310 (diol:triol relative molar ratio 0.9:1) were mixed with 0.9 cc of toluene diisocyanate and 0.05 g of stannous octoate. The molar ratio of the T.D.I. to the polyols was about 90%. The mixed reactants were coated onto a film of polyester 0.001 inch (0.025 mm) thick and cured at 150°C. for 15 minutes. The resultant cured adhesive had good pressure-sensitive adhesive properties and had an average chain length of 96 chain atoms.

EXAMPLE 2

3.15 grams of ethylene oxide capped propylene oxide diol of molecular weight 2000 and 1.13 grams of an ethylene oxide triol of molecular weight 310 (diol:triol relative mole ratio 0.4:1) were mixed with 0.9 cc of T.D.I. and 0.05 g of stannous octoate. The molar proportion of the T.D.I. to the polyols was again about 90%. The mixed reactants were coated onto polyester as indicated in Example 1 and then cured at 80°C. for 10 minutes. The resultant adhesive had good pressure-sensitive adhesive properties and had an average chain length of 74 chain atoms.

WHAT WE CLAIM IS:—

1. A pressure-sensitive adhesive comprising a partially cross-linked polyurethane reaction product between one or more diols and/or higher polyols, terminated with primary and/or secondary hydroxyl groups, and an organic polyisocyanate used in less than a stoichiometric amount the chain length of the polyurethane reaction product being less than 130 chain atoms.
2. A pressure-sensitive adhesive as claimed in claim 1 wherein the polyurethane reaction product chain length is from 38 to 125 chain atoms.
3. A pressure-sensitive adhesive as claimed in claim 1 or 2 wherein the polyurethane reaction product is produced by using not less than 80% of the stoichiometric amount of polyisocyanate.
4. A pressure-sensitive adhesive as

claimed in claim 3 wherein from 85% to 95% of the stoichiometric amount of polyisocyanate is used.

- 5 5. A pressure-sensitive adhesive as claimed in any one preceding claim wherein the polyisocyanate is TDI.
- 10 6. A pressure-sensitive adhesive as claimed in any one preceding claim wherein the polyurethane reaction product is formed using a metal carboxylate as a catalyst.
- 15 7. A pressure-sensitive adhesive as claimed in any one preceding claim wherein a mixture of diol and triol is used to form the polyurethane reaction product.
- 20 8. A pressure-sensitive adhesive as claimed in claim 7 wherein a mixture of diol of molecular weight 1000—3000 and triol of molecular weight 300—600 is used to form the polyurethane reaction product.
9. A pressure-sensitive adhesive as claimed in claim 1 and substantially as here-

in described in any Example.

10. A pressure-sensitive adhesive material consisting of the adhesive as claimed in any one preceding claim coated on to a suitable substrate. 25

11. A pressure-sensitive adhesive material as claimed in claim 11 wherein the substrate is a tape of polymer film.

12. A method of producing a pressure-sensitive adhesive material as claimed in claim 10 wherein the said one or more diols and/or higher polyols and the said polyisocyanate, together with any catalyst are applied as amixture to at least one surface of the substrate and caused or allowed to cure. 30 35

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In one aspect the present invention provides a pressure-sensitive adhesive comprising a partially cross-linked polyurethane reaction product between one or more diols and/or higher polyols, preferably triols, terminated with primary and/or secondary hydroxyl groups and an organic polyisocyanate, preferably diisocyanate used in less than a stoichiometric amount, the chain length of the polyurethane reaction product being less than 130 chain atoms.

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While any chain length below 130 is possible a chain length of 38—125 chain atoms gives useful results.

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SEE ENCL-1A SUP ATTACHED

dibutyl tin dilaurate, stannous octoate or lead octoate.

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Curing times will generally range from 3 to 20 minutes and temperatures from 60° to 200°C.

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Another aspect of the present invention is a pressure-sensitive adhesive material consisting of the adhesive as described above coated onto a suitable substrate, e.g. of fabric, paper or (especially) polymer film, particularly when this is in the form of a tape.

Yet another aspect of the invention is constituted by a method of producing such a pressure-sensitive material wherein said one or more diols and/or higher polyols and the said polyisocyanate, together with any catalyst are applied as a mixture to at least

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Usually at least 80% e.g. 85%—95% of the said stoichiometric amount will be used in the practice of this invention.

While any chain length below 130 is possible a chain length of 38—125 chain atoms gives useful results.

The preferred polyisocyanate is the toluene diisocyanate known as TDI. This is a mixture of the 2,4- and 2,6- isomer. Other aliphatic or aromatic polyisocyanates e.g. 4,4'-diisocyanatodiphenylmethane, hexamethylene diisocyanate, triphenylmethyl triisocyanate, 2,4,4'-triisocyanatotriphenyl ether and polymethylene polyphenyl isocyanate can also be utilised.

Usually a catalyst, i.e. accelerator, such as a metal carboxylate is added to the reaction mixture prior to curing. Examples are

THE FOLLOWING SLIP ATTACHED

dibutyl tin dilaurate, stannous octoate or lead octoate.

The polyols employed in this invention may be hexols, e.g. sorbitol, pentols, e.g. arabitol, tetrols, e.g. pentaerythritol, or triols, e.g. glycerol. Also, reaction products of these polyols and propylene oxide and/or ethylene oxide may be used in place of the unmodified polyols, a typical triol being a reaction product of glycerol and propylene oxide. Examples of diols which can be employed are poly(ethylene glycol) and poly(propylene glycol).

The proportion of reactants giving optimum pressure-sensitive adhesive properties depends partly on the particular diols and triols employed, especially with reference to whether the termination is by primary or secondary hydroxyl. One surprising feature which has been noted is that a different diol:triol balance is needed to generate a particular chain atom length, depending on whether the polyols are primary or secondary hydroxyl terminated. In general the chain atom length, corresponding to the degree of chain branching, will be regulated by using as polyol a corresponding proportion of diol and triol, the diol suitably having a molecular weight of 1000—3000 and the triol a molecular weight of 300—600. Under such conditions the higher the diol:triol molar ratio, other things being equal, the higher the chain length. In general, a molar ratio of diol to triol of 2:1 and below is useful for chain lengths below 130. However, using triol alone it has been found that a satisfactory product of the desired chain atom length can be formed using triols of substantially higher molecular weight.

Curing times will generally range from 3 to 20 minutes and temperatures from 60° to 200°C.

Polyols terminated with primary hydroxyl groups have the particular advantage in the process of this invention that in the presence of the organo-tin catalyst and at a temperature of 80°C, reaction speed with TDI is such that the reaction can be completed in about 10 minutes after which time no further free isocyanate can be detected by I.R. spectroscopy.

Another aspect of the present invention is a pressure-sensitive adhesive material consisting of the adhesive as described above coated onto a suitable substrate, e.g. of fabric, paper or (especially) polymer film, particularly when this is in the form of a tape.

Yet another aspect of the invention is constituted by a method of producing such a pressure-sensitive material wherein said one or more diols and/or higher polyols and the said polyisocyanate, together with any catalyst are applied as a mixture to at least

one surface of the substrate and caused or allowed to cure.

One advantage of this method is that continuation of the polymer formation will then take place on the substrate without the need for solvent recovery. Another advantage is that pressure-sensitive adhesives can readily be produced which do not require the addition of tackifying resins.

The following Examples illustrate how the invention may be carried into effect:

EXAMPLE 1

3.15 grams of ethylene oxide capped pro-molecular weight 2000 and 0.91 grams of a propylene oxide triol of molecular weight 310 (diol:triol relative molar ratio 0.9:1) were mixed with 0.9 cc of toluene diisocyanate and 0.05 g of stannous octoate. The molar ratio of the T.D.I. to the polyols was about 90%. The mixed reactants were coated onto a film of polyester 0.001 inch (0.025 mm) thick and cured at 150°C. for 15 minutes. The resultant cured adhesive had good pressure-sensitive adhesive properties and had an average chain length of 96 chain atoms.

EXAMPLE 2

3.15 grams of ethylene oxide capped propylene oxide diol of molecular weight 2000 and 1.13 grams of an ethylene oxide triol of molecular weight 310 (diol:triol relative mole ratio 0.4:1) were mixed with 0.9 cc of T.D.I. and 0.05 g of stannous octoate. The molar proportion of the T.D.I. to the polyols was again about 90%. The mixed reactants were coated onto polyester as indicated in Example 1 and then cured at 80°C. for 10 minutes. The resultant adhesive had good pressure-sensitive adhesive properties and had an average chain length of 74 chain atoms.

WHAT WE CLAIM IS:—

1. A pressure-sensitive adhesive comprising a partially cross-linked polyurethane reaction product between one or more diols and/or higher polyols, terminated with primary and/or secondary hydroxyl groups, and an organic polyisocyanate used in less than a stoichiometric amount the chain length of the polyurethane reaction product being less than 130 chain atoms.
2. A pressure-sensitive adhesive as claimed in claim 1 wherein the polyurethane reaction product chain length is from 38 to 125 chain atoms.
3. A pressure-sensitive adhesive as claimed in claim 1 or 2 wherein the polyurethane reaction product is produced by using not less than 80% of the stoichiometric amount of polyisocyanate.
4. A pressure-sensitive adhesive as

claimed in claim 3 wherein from 85% to 95% of the stoichiometric amount of polyisocyanate is used.

- 5 5. A pressure-sensitive adhesive as claimed in any one preceding claim wherein the polyisocyanate is TDI.

- 10 6. A pressure-sensitive adhesive as claimed in any one preceding claim wherein the polyurethane reaction product is formed using a metal carboxylate as a catalyst.

7. A pressure-sensitive adhesive as claimed in any one preceding claim wherein a mixture of diol and triol is used to form the polyurethane reaction product.

- 15 8. A pressure-sensitive adhesive as claimed in claim 7 wherein a mixture of diol of molecular weight 1000—3000 and triol of molecular weight 300—600 is used to form the polyurethane reaction product.

- 20 9. A pressure-sensitive adhesive as claimed in claim 1 and substantially as here-

in described in any Example.

10. A pressure-sensitive adhesive material consisting of the adhesive as claimed in any one preceding claim coated on to a suitable substrate. 25

11. A pressure-sensitive adhesive material as claimed in claim 11 wherein the substrate is a tape of polymer film.

12. A method of producing a pressure-sensitive adhesive material as claimed in claim 10 wherein the said one or more diols and/or higher polyols and the said polyisocyanate, together with any catalyst are applied as amixture to at least one surface of the substrate and caused or allowed to cure. 30 35

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